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A Review of Standards of Performance for New Stationary Sources Petroleum Refineries

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by

Kris Barrett and Alan Goldfarb

Metrek Division of the MITRE Corporation
1820 Dolley Madison Boulevard
McLean, Virginia 22102

Contract No. 68-02-2526

EPA Project Officer: Thomas Bibb

Emission Standards and Engineering Division

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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1.0 EXECUTIVE SUMMARY

New Source Performance Standards (NSPS) for petroleum refineries were promulgated by the Environmental Protection Agency (EPA) on March 8, 1974. These standards regulate the emission of particulate matter and carbon monoxide, and the opacity of flue gases from fluid catalytic cracking (FCC) unit catalyst regenerators and FCC unit regenerator incinerator-waste heat boilers. They also regulate the emission of sulfur dioxide from fuel gas combustion devices. These regulations apply to any affected facility which commenced construction or modification after June 11, 1973.

The objective of this report is to review the New Source Performance Standard (NSPS) for petroleum refineries in terms of the impact of new developments in control technology, industry operating conditions, process changes, and other issues that have evolved since the standards were promulgated. Possible revisions to the standard, based on NSPS compliance test results, are also analyzed. The following paragraphs summarize the results and conclusions of the analysis, as well as recommendations for future action.*

1.1 Particulate Matter

The current NSPS for particulate matter emissions were based on electrostatic precipitator technology. The use of multi-stage cyclones in conjunction with an electrostatic precipitator is still considered the best demonstrated control technology. A number of

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*This report reflects information and data available in June 1978.

refineries are using high-efficiency separators to reduce particulate matter loading prior to energy recovery in an expander turbine. This is then followed by a precipitator. Bag filters and venturi scrubbers can also be used on a FCC unit regenerator exhaust gas stream.

Only one NSPS compliance test was available for analysis during this task. The three test runs had a range of emission values from 0.76 to 1.35 kg particulate matter/kg coke burn-off with an average of 1.01 kg/kg coke burn-off (NSPS = 1.0 kg/kg). Based on this one compliance test and previous data from tests performed to support the standard, no change to the present particulate matter standard is recommended.

Technological advances in catalysts, temperature of regeneration and catalyst-to-feed ratios have had the effect of reducing particulate matter mass emission rates. However, the allowable emission is based on coke burn-off in the regenerator, not mass rate. Therefore, the new technologies which reduce coke formation and therefore coke burn-off, also reduce the allowable emissions in total kg of particulate matter emitted per hour. This has required the industry to increase control of the emission of entrained catalyst.

Technological advances in controls are limited to new, high-efficiency third-stage cyclones or separators. Use of a third-stage separator may control the effect of increased emissions with time due to erosion of the regenerator internal cyclones. Use of a separator to control turbine blade erosion is mandatory if energy recovery from

an expander turbine is incorporated in the FCC unit regenerator flue gas stream.

The available compliance test report included an appendix describing a problem with EPA Reference Method 5 for measuring particulate matter due to condensable sulfates. Because this method is the key to defining particulate matter and it determines the compliance/noncompliance of an affected facility, it is recommended that Reference Method 5, as it applies to catalyst regenerator emissions, be reevaluated.

An additional recommendation for the particulate matter standard is to require that the opacity be measured at the same time the mass emission is measured. This requirement will provide much needed data and will ensure that the opacity standard is consistent with the mass emission limit.

1.2 Carbon Monoxide

The best demonstrated control technology for carbon monoxide (CO) is considered to be the carbon monoxide incinerator-waste heat boiler. No compliance test data were available for carbon monoxide emissions from FCC unit regenerators using controls other than carbon monoxide boilers. These incinerator waste heat boilers are capable of reducing the emission of CO to 0 to 14 ppm, far below the current standard of 500 ppm. The standard was established at 500 ppm to permit control of CO emissions by regenerator in-situ oxidation. There is no data to substantiate the level of CO emissions from

regenerators using in-situ oxidation other than journal statements of "less than 500 ppm." Approximately 20 percent of the U.S. regenerators are operating with CO oxidation promoters (Wallendorf, 1978). It is recommended that data be collected to ascertain the capabiliy of these systems to reduce CO and the level of reduction possible, then reevaluate the CO standard based on this new data.

1.3 Sulfur Dioxide

Sulfur dioxide emissions from fuel gas combustion devices can be controlled by reducing the hydrogen sulfide content of the fuel gas or by flue gas desulfurization (FGD). The standard was written to limit the H_2S content of fuel gas, although the owner/operator has the option of using FGD. The available compliance test data indicate that: (1) all NSPS affected facilities identified chose to limit the H_2S content of fuel gas instead of using FGD, and (2) the technology for reducing H_2S concentrations substantially below the present NSPS limit is being used. There is no data to show the effect of the increased sulfur content of feedstock expected with increased imports. This relationship should be considered before a decision is made on whether the standard can be changed to reduce the allowable H_2S content of fuel gas.

Another recommendation is to change the definition of a fuel gas combustion device so that a regenerator incinerator-waste heat boiler is no longer excluded from compliance with the SO_x standard. The original rationale for excluding the boiler from the standard, even

when using fuel gas as an auxiliary fuel, is not known. A third recommendation concerns the monitoring of hydrogen sulfide in fuel gas. The lack of a continuous monitoring method for H_2S has been reported by EPA Regional personnel as a weakness in the current NSPS (Watson et al., 1978).

There is currently no NSPS for sulfur dioxide emissions from the FCC unit regenerator/regenerator incinerator-waste heat boiler. Arthur D. Little, Inc. (1976) has estimated that a SO_x flue gas control level of 300 ppm or 500 ppm will reduce emissions by 85,000 tons/year and 49,000 tons/year respectively by 1985. This is a reduction from their estimate of 480,000 tons/year of SO_x emitted by FCC units in 1985. It is recommended that further analysis be done to determine if a suitable standard can be developed and that this standard include an additional sulfur dioxide allowance for regenerator incinerator-waste heat boilers using auxiliary liquid or solid fossil fuels.

1.4 Hydrocarbons

The emission of hydrocarbons of concern to public health officials from uncontrolled FCC unit regenerators has been established by Radian Corporation (Bombaugh et al., 1976). The actual emissions released under differing operating conditions or control equipment have not been determined. Arthur D. Little, Inc. (1976) has stated that the emission of hydrocarbons is negligible when using either a CO boiler or high temperature regeneration (HTR). New CO oxidation

promoters can reduce the temperature at which effective HTR can be carried out and the emissions from a regenerator under these conditions are unknown. It is recommended that data be collected to ascertain the need for a NSPS for hydrocarbon emissions.

2.0 INTRODUCTION

2.1 Purpose and Scope

On March 8, 1974, the Environmental Protection Agency promulgated New Source Performance Standards (NSPS) for Petroleum Refineries (39 FR 9315). Revisions were made on October 6, 1975 (40 FR 46250) and again on July 25, 1977 (42 FR 37937). These standards establish emissions limits and require emission testing; monitoring; and reporting for particulate matter, opacity, and carbon monoxide from fluid catalytic cracking unit regenerators, and sulfur dioxide from fuel gas combustion devices.

The Clean Air Act Amendments of 1977 require that the Administrator of the EPA review, and if appropriate, revise established standards of performance for new stationary sources at least every four years (Section 111(b)(1)(B)). This report includes reviews of the current standards, the status of current applicable control technology, and the ability of petroleum refineries to meet the current standards. The compliance test results, information retrieved from the literature, and discussions with industry representatives form the basis for analyses of the current standards to determine if they are sufficient, too stringent, or not stringent enough. The problems associated with the monitoring requirements of the standards were analyzed, and recommendations are made concerning specific changes or studies to be conducted. Also discussed are problems at

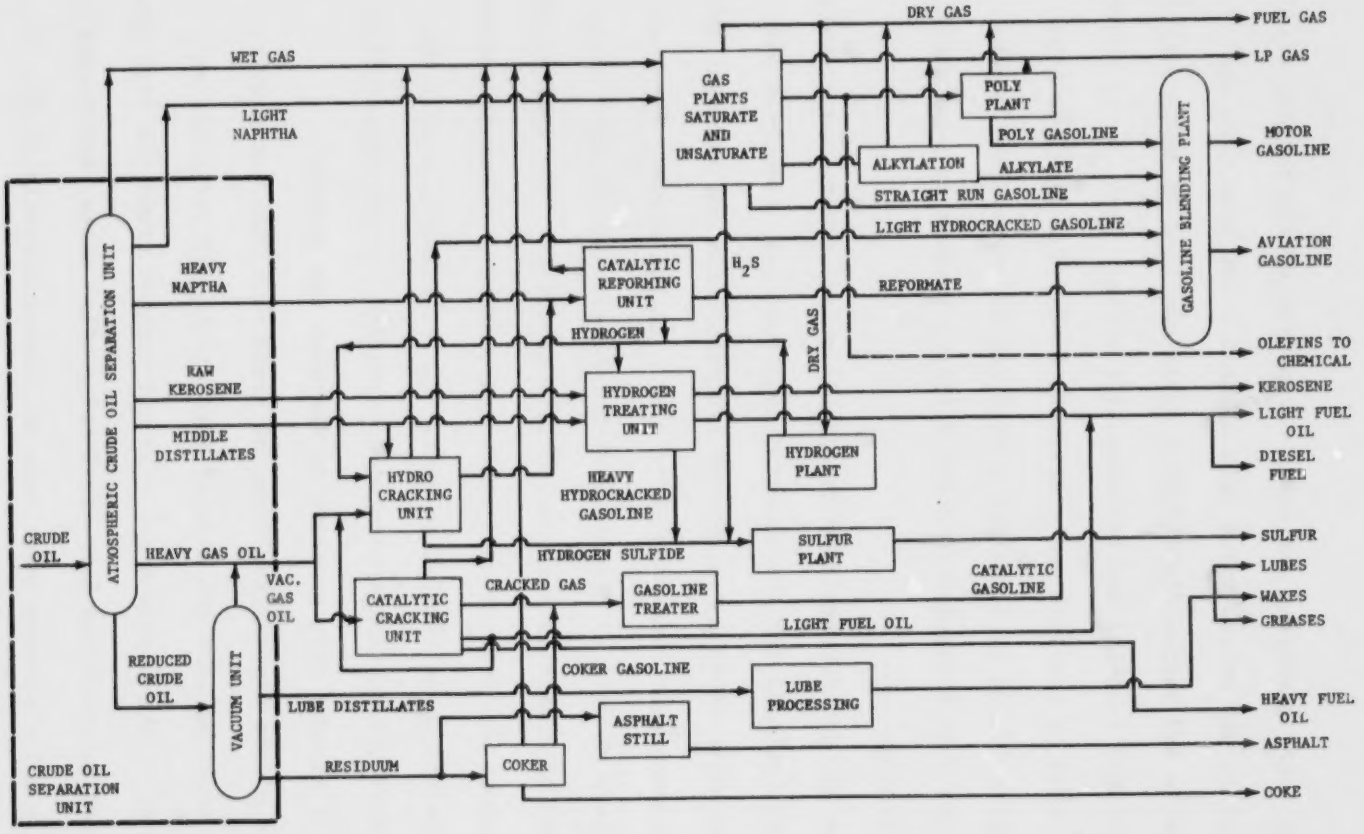
petroleum refineries that relate directly to the environmental pollution load emitted and that may affect present or future NSPS.

2.2 Background Information

A petroleum refinery transforms crude oil into a variety of useful products. The petroleum refining industry produces more than 2500 products that can be categorized into the following classes: fuel gas, gasoline, kerosine, fuel oil, lubricating oil, grease, wax, asphalt, coke, chemicals, and solvents. There is no "typical" refinery, since the number of products and the product mix varies widely within a refinery as well as between refineries. The manufacturing processes also vary depending on refinery age, type of technology, capacity, location, and type of crude processed.

Petroleum refinery operations involve physical separation of components of the crude oil (e.g., crude distillation) and chemical conversion processes which transform some of the less useful components of the oil into more useful products (e.g., cracking of high molecular weight oils into lower molecular weight products such as gasoline).

The processing sequence of a modern refinery is illustrated in Figure 2-1. The crude oil is heated and charged to an atmospheric distillation tower where it is separated into several light, intermediate, and heavy fractions. The bottoms from the tower are sent to a vacuum distillation unit for further separation. The bottoms from the vacuum still are thermally cracked in a coker to produce a



Source: Laster, 1973.

FIGURE 2-1
PROCESSING PLAN FOR COMPLETE MODERN REFINERY

wet gas, coker gasoline, and coke. A portion of the bottoms from the vacuum still may be processed into asphalt. Gas oils from the atmospheric and vacuum distillation units are used as feedstocks for the catalytic cracking and hydrocracking units. These units convert the gas oils to gasoline and distillate fuel. The gasoline from these units is fed to a catalytic reformer to improve the octane number and then blended with other refinery streams to make gasolines for marketing.

The wet gas streams from the distillation, coker, and cracking units are combined and fractionated into fuel gas, liquified petroleum gas, and unsaturated and saturated branched chain and straight chain, light hydrocarbons containing from 3 to 5 carbon atoms. The fuel gas is used as fuel in the refinery furnaces. The straight chain saturated hydrocarbons are blended into gasoline. The unsaturated hydrocarbons and the branched chain hydrocarbons, primarily isobutane, are processed in an alkylation unit. In the alkylation unit the unsaturated hydrocarbons react with isobutane to form isoparaffins which are blended into gasoline to increase the octane.

The middle distillates from the crude unit, the coker unit, and the cracking unit are blended into diesel and jet fuels and furnace oil. Heavy vacuum gas oils and reduced crude oil from some crudes can be processed into lubricating oils, waxes, and grease.

Only a few process units emit pollutants directly to the atmosphere--the catalytic cracking unit, the coker, and the process

heaters. Pump seals, valves, relief vents, leaks, and sampling operations are sources of fugitive emissions. Air pollutants that may be released into the environment from a refinery, and some of the sources of these emissions, are summarized in Table 2-1.

2.2.1 Catalytic Cracking Units

Catalytic cracking is a process for converting heavy oils into more valuable gasoline and lighter products. Almost 5 million barrels of oil are processed daily in catalytic cracking units in the U.S. Originally, cracking was accomplished thermally, but catalytic processes have almost completely replaced thermal cracking because of the improved yield and quality of the product from the catalytic process. Three types of catalytic cracking processes have been used: the fixed bed (Houdry process), the moving bed (Thermofor process), and the fluidized bed.

The fixed bed process is considered obsolete, and only three refineries still use this process. The moving bed process is being phased out and only 16 refineries use this method.

There are 122 fluidized bed catalytic cracking units currently operating with the capability of processing 4.7 million barrels of oil daily. During the next 2 years an additional 16 fluid bed catalytic crackers are scheduled to be placed in operation. The combined capacity of these units is approximately 321,000 barrels of oil per day. However, this figure does not represent increased capacity, since some units may replace existing older units. Also,

TABLE 2-1

POTENTIAL SOURCES OF ATMOSPHERIC EMISSIONS WITHIN REFINERIES

Type of Emission	Source
Particulates	Catalytic Cracker, Fluid Coking, Catalyst Regeneration, Process Heaters, Boilers, Decoking Operations, Incinerators
Sulfur Oxides	Sulfur Recovery Unit, Catalytic Cracking, Process Heaters, Boilers, Decoking Operations, Unit Regenerations, Treating Units, Flares
Nitrogen Oxides	Process Heaters, Boilers, Catalyst Regeneration, Flares
Hydrocarbons	Storage Tanks, Loading Operations, Water Treating, Catalyst Regeneration, Barometric Condensers, Process Heaters, Boilers, Pumps, Valves, Blind Changing, Cooling Towers, Vacuum Jets
Carbon Monoxide	Catalyst Regeneration, Decoking, Compressor Engines, Incinerators
Odors	Treating Units, Drains, Tank Vents, Barometric Condensers, Sumps, Oil-Water Separators

Source: Dickerman, et al., 1977.

although some units represent additions to refinery capacity, this figure represents the total capacity of the refinery after the addition.

The fluidized catalytic cracking (FCC) process uses a catalyst in the form of fine particles that are fluidized with a vapor. The fluidized catalyst is continuously circulated between a reaction zone and a regeneration zone. Two types of FCC units are commonly used. In the "side-by-side" type, the reaction and regeneration chambers are separate vessels next to each other. In the stacked type, the reactor is mounted on top of the regenerator and the two vessels appear as one when viewed externally. Other variations in FCC design and operation relate to the type of catalyst employed and the design of the catalyst transfer line between the regenerator and the reactor. However, the operating principles of the various FCC reactors are essentially the same.

A schematic diagram of a fluid catalytic cracking unit is shown in Figure 2-2. In operation, the gas oil is fed to the bottom of the riser pipe where it joins the hot, regenerated catalyst. The fuel is vaporized and flows upward along with the catalyst particles. The cracking reaction takes place in the riser. Because the reaction is endothermic, cooling of the reacting mixture occurs as it rises into the reactor. The product gases exit through the top of the separator and the catalyst particles drop into the stripper section where they are blown with steam to strip hydrocarbons that are

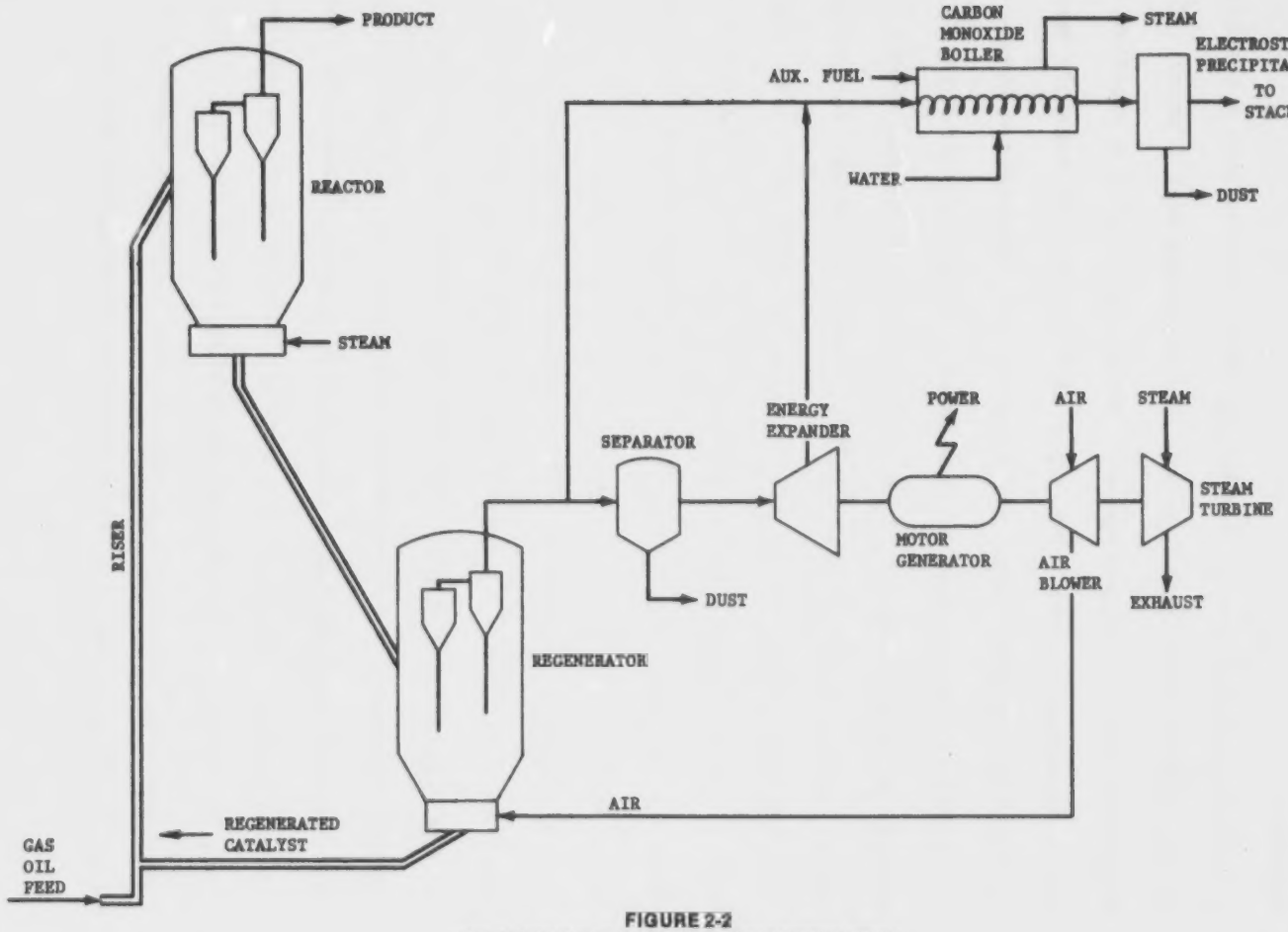


FIGURE 2-2
MODERN FLUID CATALYTIC CRACKING UNIT
WITH CONTROLS AND ENERGY RECOVERY

entrained on the catalyst. During the cracking process, the catalyst loses its activity due to the formation of coke deposits. In order to restore the catalytic activity, the spent catalyst is passed into a regenerator where the coke is burned off in a controlled combustion process with prcheated air. The hot regenerated catalyst then flows to the bottom of the riser to mix with incoming gas oil feed and the cycle is repeated.

The products of combustion are vented through the top of the regenerator. The regenerator vent gases contain particulate matter from entrained catalyst, sulfur oxides from sulfur retained in the coke, carbon monoxide from incomplete combustion of coke, hydrocarbons, nitrogen oxides, aldehydes, and ammonia. Table 2-2 lists emission factors for each of these pollutants discharged from an uncontrolled fluid bed catalyst regenerator along with the potential nationwide emissions based on the current capacity of fluidized bed catalytic reactors in the U.S.

2.2.2 Description of Fuel Gas Combustion Device

Fuel gas is produced in a refinery from a wide variety of process operations including: crude oil separation, catalytic cracking, hydrocracking, coking, and reforming. The gas is treated and then used in process heaters, boilers, flares, and various other places in the refinery. A fuel gas combustion device is quite literally any equipment in a petroleum refinery that is used to burn fuel gas. Fluid coking units, fluid catalytic cracking unit incinerator-waste

TABLE 2-2

NATIONWIDE FLUIDIZED BED CATALYTIC CRACKER REGENERATOR EMISSIONS, UNCONTROLLED

Pollutant	Emission Factor (kg/m^3 fresh fuel)[a]	Estimated Maximum Daily Emission (kg)[b]	Estimated Annual Emission (kg)[b]
Particulates	0.267 - 0.976	$2.1 \times 10^5 - 7.7 \times 10^5$	$6.9 \times 10^7 - 2.5 \times 10^8$
Sulfur Oxides	0.898 - 1.505	$7.1 \times 10^5 - 1.2 \times 10^6$	$2.3 \times 10^8 - 3.9 \times 10^8$
Carbon Monoxides	39.2	3.1×10^7	1.0×10^{10}
Hydrocarbons	0.630	5.0×10^5	1.6×10^8
Nitrogen Oxides	0.107 - 0.416	$8.4 \times 10^4 - 3.3 \times 10^5$	$2.8 \times 10^7 - 1.1 \times 10^8$
Aldehydes	0.054	4.3×10^4	1.4×10^7
Ammonia	0.155	1.2×10^5	4.0×10^7

[a]U.S. EPA, 1973.

[b]Calculated from capacity data reported in Cantrell, 1978.

heat boilers, and facilities that burn fuel gas to produce sulfur or sulfuric acid are excluded from the NSPS definition of a fuel gas combustion device. Flue gases from these sources are vented to the atmosphere with or without heat recovery and/or treatment.

3.0 CURRENT STANDARDS FOR PETROLEUM REFINERIES

3.1 Facilities Affected

The NSPS for petroleum refineries are applicable to fluid catalytic cracking unit catalyst regenerators, fluid catalytic cracking unit regenerator incinerator-waste heat boilers, and fuel gas combustion devices that commenced construction or modification after June 11, 1973.

The following terms are pertinent to the determination of the applicability of the NSPS to a facility.

- A petroleum refinery is any facility engaged in producing gasoline, kerosene, distillate fuel oils, residual fuel oils, lubricants, or other products through distillation of petroleum or through redistillation, cracking or reforming of unfinished petroleum derivatives.

- Construction is the fabrication, erection, or installation of an affected facility, or any apparatus to which a standard is applicable. This includes construction that is completed within an organization as well as the more common situation in which the facility is designed and constructed by a contractor.

- A modification is any physical change in, or change in the method of operation of, an existing facility which increases the amount of any air pollutant (to which a standard applies) emitted into the atmosphere by that facility or which results in the emission of any air pollutant (to which a standard applies) not previously emitted into the atmosphere. However, increases in production rates up to design capacity, relocation or change in ownership of an existing facility, and fuel switches if the equipment was originally designed to accommodate such fuels, are not considered to be modifications.

- Reconstruction is the replacement of components of a facility to such an extent that the capital costs of the new components is greater than 50 percent of the capital costs of a comparable entirely new facility. After replacement, the facility must be technologically and economically capable of complying with the NSPS. If a facility meets these criteria, it is designated an affected facility, regardless of any changes in the rate of emissions.

3.2 Pollutants Controlled

The NSPS for petroleum refineries regulate the emission of:

- particulate matter from FCC unit catalyst regenerators or FCC unit regenerator incinerator-waste heat boilers,
- carbon monoxide from FCC unit catalyst regenerators, and
- sulfur dioxide from fuel gas combustion devices.

3.2.1 Standard for Particulate Matter

The standard for particulate matter has been set at 1.0 kg/1,000 kg (1.0 lb/1,000 lb) of coke burn-off in the catalyst regenerator. In addition, no gases are to be emitted that exhibit greater than 30 percent opacity except for one six-minute average opacity reading in any one-hour period.

In those instances in which auxiliary liquid or solid fossil fuels are burned in the FCC unit regenerator incinerator-waste heat boiler, the incremental rate of particulate matter emissions may exceed the above, but not exceed 0.18 g/million cal (0.10 lb/million Btu) of heat input attributable to the auxiliary liquid or solid fuel.

3.2.2 Standard for Carbon Monoxide

The standard for carbon monoxide restricts emissions to no greater than 0.050 percent by volume of carbon monoxide in gases discharged from a FCC unit catalyst regenerator.

3.2.3 Standard for Sulfur Dioxide

The standard for sulfur dioxide applies to any fuel gas combustion device. These devices are defined as any equipment used to burn fuel gas, such as process heaters, boilers, and flares. Fluid coking units, FCC unit incinerator-waste heat boilers, and facilities in which gases are burned to produce either sulfur or sulfuric acid are not included.

The standard prohibits the burning of fuel gas containing in excess of 230 mg H_2S/dscm (0.10 gr/dscf) in any fuel gas combustion device, except as discussed below. The combustion of process upset gas in a flare, and process gas or fuel gas released to a flare from relief valve leakage is exempt from this standard.

The alternative to the 230 mg H_2S/dscm fuel gas standard is that an owner or operator may elect to treat the gases resulting from the combustion of fuel gas so as to limit the release of SO_2 to the atmosphere. The EPA Administrator must be satisfied that treating of the combustion gases controls SO_2 emissions as effectively as compliance with the H_2S standard.

3.3 Monitoring and Reporting Requirements

Continuous monitoring is required for opacity, carbon monoxide, and sulfur dioxide. The regulations require owners or operators to install, calibrate, maintain, and operate a continuous monitoring system for the opacity of emissions from FCC unit catalyst regenerators. The opacity monitoring system is to be spanned at 60, 70, or 80 percent opacity.

The continuous monitoring of carbon monoxide emissions from FCC unit catalyst regenerators will be required on all NSPS affected facilities as soon as instrument specifications are promulgated by EPA. This will require a retrofit of instruments on affected facilities already in place.

A continuous monitoring system is required for the measurement of sulfur dioxide in the gases discharged to the atmosphere from the combustion of fuel gases. Calibration checks are made using SO_2 as the calibration gas. The span is set at 100 ppm. Reference Method 6 is used for conducting monitoring system performance evaluations. This continuous monitoring system is not required where a continuous monitoring system for the measurement of hydrogen sulfide is installed. The EPA has not yet developed performance specifications for hydrogen sulfide continous monitoring systems. Therefore, owners and operators electing to monitor H_2S are effectively exempt from the SO_2 monitoring requirements (40 FR 46250) until EPA establishes instrument performance specifications for an H_2S monitor.

The average coke burn-off rate (thousands of kilograms/hour) and hours of operation for any FCC unit catalyst regenerator are required to be recorded daily. Computation of the coke burn-off rate is done using the formula in 40 CFR 60.106(4).

Owners and operators of FCC unit catalyst regenerators who use an incinerator-waste heat boiler to burn the regenerator exhaust gases are required to record the daily rate of combustion of liquid

or solid fossil fuels (liters/hour or kilograms/hour) and the hours of operation during which these fuels are burned in the boiler.

The reports required for NSPS affected facilities are submitted to the EPA Administrator for every calendar quarter within 30 days of the end of the quarter.

The following reports of excess emissions are required:

- opacity - all one-hour periods that contain two or more six-minute periods during which the average opacity exceeds 30 percent as measured by the continuous monitoring system, and
- sulfur dioxide - any six-hour period during which the average (arithmetic average of six contiguous one-hour periods) emissions of SO_2 exceed the standard as measured by the continuous monitoring system.

4.0 STATUS OF CONTROL TECHNOLOGY

4.1 Scope of Industrial Operations

4.1.1 Distribution of Sources

There are 285 operating petroleum refineries in the U.S. with a total capacity of nearly 18 million barrels of crude oil per stream day. The largest number of refineries are located in EPA Region VI (37 percent of total refineries and 45 percent of total capacity). Texas, California, and Louisiana are the three largest refinery states with 19, 14, and 8 percent of the refineries and 27, 14, and 12 percent of the capacity, respectively.

The fluid catalytic cracker is an essential part of the modern refinery. Nearly one-half of all refineries have FCC units as part of their process. Table 4-1 shows the distribution of these fluid catalytic cracking units by EPA Region. EPA Regions V and VI contain 53 percent of the FCC equipped refineries and 62 percent of the refinery FCC unit capacity. Texas, Louisiana, and California are the states with the largest FCC unit capacity (Cantrell, 1978).

4.1.2 Industry Growth Pattern

The growth of the petroleum refinery industry has been affected by government regulation of fuel prices and the oil embargo. According to data presented in the Oil and Gas Journal (Cantrell, 1978), 27 new refineries have been built between 1975 and 1978. Thirteen of these refineries were built in EPA Region VI. Although the actual number of new FCC units built in the same period is unknown, capacity was

TABLE 4-1

GEOGRAPHIC DISTRIBUTION OF FLUID CATALYTIC CRACKER UNITS

Region	Number of Refineries		Fluid Catalytic Cracker Units				
			Number of Refineries With FCCU	Capacity[a]		Percent of Total	
	1978	75-78	1978	1978	75-78	Number	Capacity
I	1	-	-	-	-	-	-
II	7	-	3	197	10	2	4
III	16	(1)[b]	6	309	15	5	7
IV	20	5	3	120	-	2	3
V	36	-	19	771	86	16	17
VI	100	13	45	2081	147	37	45
VII	13	-	16	373	(10)[b]	13	8
VIII	35	3	15	175	5	12	4
IX	44	5	13	509	111	11	11
X	13	1	2	66	3	2	1
Total	285	26	122	4600	368	100	100

Sources: Cantrell, 1975; 1978.

[a] Capacity in 10^3 barrels per stream day.

[b] Reduction in number of refineries or capacity.

increased by 368,000 barrels per stream day. A distribution of this growth in FCC unit capacity is shown in Table 4-1.

The data from the Oil and Gas Journal (Cantrell, 1978) on increased capacity of FCC units show that 50 refineries have built new FCC units or expanded FCC unit capacity during the period 1975-1978. It is not within the scope of this report to make a determination on how many of these units are affected facilities and subject to the NSPS. During interviews with each EPA Regional office, only two FCC units were reported as subject to NSPS. (Data from EPA Region IX were not received.)

In Table 4-2, data from Hydrocarbon Processing (1978) are presented to show a planned growth in seventeen FCC units during the period 1978-1980. Of these, six projects are under construction and eleven are in an engineering phase. Four of the units under construction are indicated as new units.

4.2 Applicable Control Technology To Meet Standards

The NSPS are based on best demonstrated control technology which is reasonable from an economic viewpoint. For this reason, a review of available control technologies used by petroleum refineries is very important. In this section, the control technologies currently used to meet the NSPS are reviewed. The technologies are discussed in the order of their prevalence in the industry.

TABLE 4-2
REPORTED PREDICTIONS OF REFINERY GROWTH 1977-1980[a]

EPA Region	Company/City	FCC	CO Boiler	Refinery
Region I				
Connecticut	None indicated			
Maine	"			
Massachusetts	"			
New Hampshire	"			
Rhode Island	"			
Vermont	"			
Region II				
New Jersey	Mobil, Paulsboro	30 Mb/d,U80		
New York	None indicated			
Region III				
Delaware	None indicated			
Maryland	Crown Central, Baltimore			200 Mb/d,E
	Stewart, Piney Point			100 Mb/d,P
Pennsylvania	Sun, Marcus Hook	Re,E		
Virginia	Hampton Roads Energy, Portsmouth			184.1 Mb/d, E80
West Virginia	None indicated			
Region IV				
Alabama	None indicated			
Florida	"			
Georgia	"			
Kentucky	"			
Mississippi	"			
North Carolina	"			
South Carolina	"			
Tennessee	Delta, Memphis	25 Mb/d,E79		

Phase: C=Completed since 9/1/77, E=Engineering, P=Planning, Re=Revamp, U=Under construction
Year: (77, 78, 79, 80)
[a] Compiled as of 1/1/78 and reported in thousand barrels/day (Mb/d)
Source: Hydrocarbon Processing, 1978.

TABLE 4-2 (Continued)
REPORTED PREDICTIONS OF REFINERY GROWTH 1977-1980[a]

EPA Region	Company/City	FCC	CO Boiler	Refinery
Region V				
Illinois	None indicated			
Indiana	Energy Coop, East Chicago	Expansion,E		
Iowa	None indicated			
Michigan	Total Petroleum, Alma	By 4 Mb/d,C77		
Minnesota	None indicated			
Wisconsin	"			
Region VI				
Arkansas	None indicated			
Louisiana	Continental, Lake Charles	30.8 Mb/d,E79		
	Good Hope, Good Hope	Ex 55 Mb/d,U		
	Gulf, Alliance	By 11 Mb/d,E79		
	Marathon, Garyville	75 Mb/d,E79		Exp.,E79
	Murphy, Meraux	25 Mb/d,E79		
	Shepherd, Jennings			10 Mb/d,U
	T&S, Mermentau			10 Mb/d,E78
New Mexico	Plateau, Bloomfield	5 Mb/d,U77		
Oklahoma	Continental, Ponca City		C	
Texas	Diamond Chamrock, Dumas	32.5 Mb/d,U79		
	La Gloria, Tyler	Re,E79		
	Phillips, Sweeny	Re,C To 190 Mb/d,E79		
	Sun, Corpus Christi	To 25 Mb/d,C		
	Texas City, Texas City	By 8 Mb/d,E78		
	Tipperary, Ingleside			5 Mb/d,C By 15 Mb/d,E78
	Uni, Rockport			10 Mb/d,E78
	Union, Nederland	Re,C		

Phase: C=Completed since 9/1/77, E=Engineering, P=Planning, Re=Revamp, U=Under construction
Year: (77, 78, 79, 80)
[a] Compiled as of 1/1/78 and reported in thousand barrels/day (Mb/d)
Source: Hydrocarbon Processing, 1978.

TABLE 4-2 (Concluded)
REPORTED PREDICTIONS OF REFINERY GROWTH 1977-1980[a]

EPA Region	Company/City	FCC	Co. Boiler	Refinery
Region VII				
Kansas	CRA, Phillipsburg	To 9 Mb/d,U79		
Missouri	None indicated			
Nebraska	"			
Ohio	"			
Region VIII				
Colorado	Gary Western, Fruita			To 10 Mb/d,U78
Montana	None indicated			
North Dakota	Amoco, Mandan		U	
South Dakota	None indicated			
Utah	"			
Wyoming	Little America, Casper	17 Mb/d,E78		
	Mountaineer, La Barge			By 4.2 Mb/d,P80
Region IX				
Arizona	None indicated			
California	Lion, Bakersfield		E78	
Hawaii	Hawaiian Independent, Barbers Point			By 7.5 Mb/d, E78
Nevada	None indicated			
Region X				
Alaska	None indicated			
Idaho	"			
Oregon	Cascade Energy, Columbia			30 Mb/d,P
Washington	United Independent, Seattle			Re,E

Phase: C=Completed since 9/1/77, E=Engineering, P=Planning, Re=Revamp, U=Under construction
Year: (77, 78, 79, 80)
[a] Compiled as of 1/1/78 and reported in thousand barrels/day (Mb/d)
Source: Hydrocarbon Processing, 1978.

4.2.1 Fluid Catalytic Cracker

The fluid catalytic cracker regenerator and regenerator waste heat boiler have NSPS for opacity, particulate matter, and carbon monoxide. Opacity and particulate matter will be discussed together since the controls are the same. Control of carbon monoxide will be discussed separately.

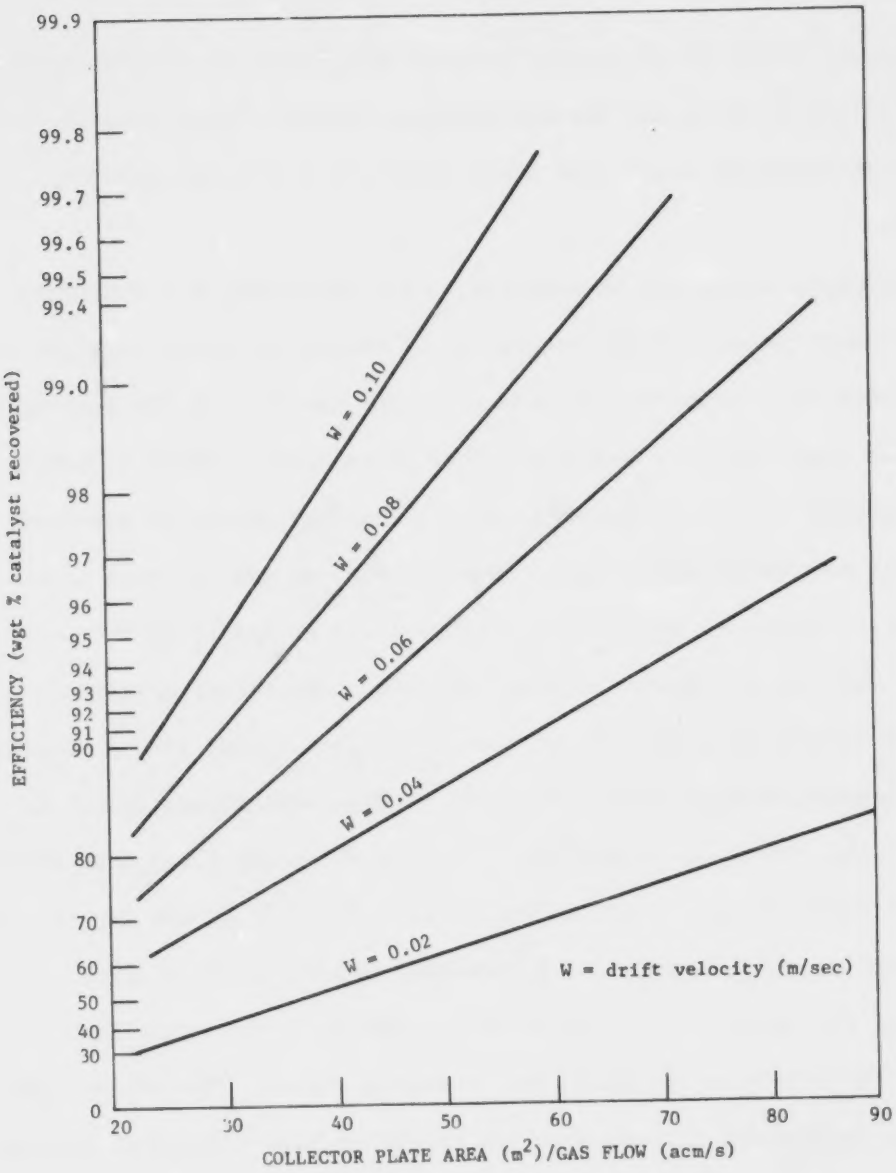
4.2.1.1 Particulate Matter Control. The present NSPS for opacity and particulate matter was based on the use of electrostatic precipitators as the best demonstrated control technology, (EPA, 1973a). Even with new innovations, electrostatic precipitators remain the best demonstrated control technology for particulate matter.

Electrostatic precipitators are fine particle agglomerators combined with a gravity settling chamber. On FCC unit regenerators, the precipitator is generally a horizontally mounted steel box containing positive electrodes and grounded plates. A corona discharge at the electrode ionizes gases which transfer their charge to the particles present. The charged particles then drift to the plates or electrodes where they agglomerate. A rapping mechanism knocks these larger, agglomerated particles free from the plates and electrodes and they settle into a gravity settling chamber or hopper from which they are collected and discarded.

The precipitator efficiency is dependent on: the effective voltage of the emitting electrodes, the resistivity of the particulate matter, the particle drift velocity, the collector plate area,

the plate rapping cycle, and the velocity, residence time and flow rate of the gas stream. The primary design parameter is the collector plate area. Operating parameters include electrode voltage adjustment, plate rapping cycle, velocity distribution, and ammonia injection to reduce particle resistivity.

Moderate changes in FCC regenerator operation will not affect the precipitator efficiency. However, changes in catalyst (affecting particle resistivity), flue gas flow, or particle size can affect efficiency significantly. Particle size is of particular importance. As particle size decreases, the efficiency of the precipitator decreases. Figure 4-1 shows the effect of particle size on the efficiency of an electrostatic precipitator. The particle drift velocity (w) is proportional to particle radius. For any given plate size, efficiency will decrease as particle size decreases. This is a very important consideration when designing precipitators for FCC regenerators built or retrofitted with modern, high efficiency cyclones and separators that can remove essentially all particulate matter greater than 15 microns in diameter (Krueding, 1975). Other parameters affecting particle drift velocity, such as electrode voltage and gas velocity are controlled to increase the drift velocity of the smaller particles. Precipitators for FCC regenerator emissions are currently designed for gas velocities of 5 to 6 feet per second and 21 to 27 feet of gas travel for 80 to 95 percent removal efficiency; gas velocities of 3 to 4 feet per second and 30 to 36 feet of



Source: American Petroleum Institute, 1978.

FIGURE 4-1
EFFECT OF PARTICLE SIZE ON COLLECTION EFFICIENCY OF AN ELECTROSTATIC PRECIPITATOR

gas travel for 95 to 99 percent removal efficiency; with a distance of 8 1/2 to 9 3/4 inches between colector plates. Plate rapping is done approximately every four hours (American Petroleum Institute, 1978).

Cyclone technology is integral to the operation of a FCC unit. The primary purpose of the cyclone is to return entrained catalyst to the fluid bed. Multiple cyclones in series are used in the reactor and the regenerator to reduce the loss of catalyst. These cyclones are internal to the process unit and, therefore, cannot be repaired without suspending operations. Deterioration of the cyclones is an important factor in determining the operating period of an FCC unit since most units operate for more than two years before shutdown.

A cyclone is a centrifugal dust collection device with a tangential opening through which a particle carrying gas stream enters a cylindrical barrel at high speed. The gas stream is given a downward spiral which forces the particles to the outer wall of the barrel and downward to a dust hopper. The "cleaned" gas stream then exits through the center of the top of the barrel while the collected particles return to the fluid bed through a dipleg. The exhaust gas stream then passes through a series of one or more additional cyclones prior to its exit from the regenerator. A thorough description of cyclone theory is beyond the scope of this report. For more complete information, refer to the Manual on Disposal of Refinery Wastes, Volume On Atmospheric Emissions (American Petroleum Institute, 1978).

There are three important factors that affect emissions from cyclones (American Petroleum Institute, 1978):

- Catalyst attrition - production of fine particles
- Particle size - particle collection efficiency decreases exponentially with decreasing particle size.
- Particle loading - particle collection efficiency increases with increased loading.

Catalyst attrition, defined as the production of fines (particles less than 44 microns in diameter), results almost exclusively from impaction of particles in the first stage cyclone rather than from the breakdown of particles in the catalyst bed. Catalyst attrition is observed in most installations, and makeup catalyst is required to maintain the fluid bed in the reactor. Losses occur through the cyclones which are incapable of collecting the fines. The bed inventory eventually reaches an equilibrium which can consist of as much as 30 weight percent less than 40 microns (American Petroleum Institute, 1978).

The particle collection efficiency of a cyclone is affected by particle size and gas stream loading. Efficiency decreases exponentially with decreases in particle size until nearly all fines less than 5 microns pass through uncollected. On the other hand, efficiency increases with gas stream loading. This can amount to as much as a 60 percent increase in efficiency in a cyclone operating at 35

percent single particle collection efficiency at no load (< 1 grain solid/cubic foot gas) when increased to a load of 1,000 grains solid/cubic foot of gas (American Petroleum Institute, 1978).

Filters have been used for the collection of particulate matter throughout the industry. There are various types and their use depends on the particular characteristics of the gas stream to be cleaned. Filters may be: flexible tubes, bags, or sheets of material; semirigid supported fabric or mats of fibrous material; fixed or packed beds of granular particles; and/or fluidized or moving beds of granules or fibers. Pertinent gas stream characteristics are particle size, temperature, moisture content, corrosivity, and flammability. Collectively, these characteristics will determine the suitability of a filter medium.

The theory of filtration for particulate matter control is that collection of particles in the micron range will take place by:

- Impaction - of the particle on the filter medium due to inertial impingement as related to gas stream velocity and particle size
- Interception - of the particle by the medium due to the size of the particle with respect to the pore size of the medium
- Diffusion - of extremely small particles due to Brownian movement which increases the probability of contact with the filter medium
- Miscellaneous - mechanisms such as electrostatic forces, thermal effects on agglomeration and Brownian movement, and sedimentation of heavy particles in low velocity gas streams due to gravity.

The filter medium can be used either under pressure or vacuum in order to maintain gas flow. As particulate matter is collected, filter efficiency increases because the collected material acts as a filter medium. As efficiency increases however, the energy required to maintain gas flow increases. A trade-off point is reached where cleaning or replacement of the medium is required.

Cleaning is achieved by gentle shaking or reverse gas flow. Beds are usually not cleaned but are replaced when the pressure drop becomes excessive.

Filters are the most efficient particulate matter control device, especially for very small (sub-micron) particles. The cost of this efficiency is relatively high however, and few filters are used on FCC unit regenerators.

Wet Scrubbers can be used to remove gaseous pollutants as well as particulate matter from flue gases. Although scrubbers are not as efficient as fabric filters, they can be used for many gaseous streams that would be unsuitable for fabric filters due to moisture content, corrosivity, temperature, or flammability. Scrubbers have disadvantages such as cost and resulting sludge disposal.

The sequence of removing particles from a gas stream by using scrubber technology can be summarized as:

- Conditioning - the particles so that a high degree of contact occurs between the particle and liquid

- Separation - of the particle/liquid from the gaseous stream using cyclones or impingement baffles
- Removal - of the particle/liquid from the scrubber, usually as a slurry that can be disposed of as is or dewatered for recirculation to the scrubber.

Comparisons of the various particulate matter control technologies have been made by the American Petroleum Institute (1978). In Table 4-3, relative cost, particle size collection, pressure drop, and energy consumption are compared for the four types of control equipment previously discussed. Filters and electrostatic precipitators are capable of removing the smallest particles, but the precipitators have a substantially lower pressure drop. Single stage cyclones, spray towers, and electrostatic precipitators have the lowest power consumption and the lowest relative cost including auxiliaries.

Data on the particle collection efficiency of the various controls are shown in Table 4-4. Fabric filters and venturi scrubbers have the highest overall efficiency (American Petroleum Institute, 1978). Many of the controls discussed show a dramatic decrease in efficiency when collecting smaller sized particles. Table 4-4 shows the particle collection efficiency of particles 5, 2, and 1 micron in diameter. It is apparent from this data that the FCC unit regenerator cyclones are incapable of significantly reducing small (<5 micron) particle emissions. The effects of dust, gas stream, and collector variables on particulate matter control equipment are

TABLE 4-3

APPROXIMATE CHARACTERISTICS OF DUST AND MIST COLLECTION EQUIPMENT

Equipment	Relative Cost[a]	Smallest Particle Collected (microns)[b]	Pressure Drop (inches of water)	Power Used (kilowatt per 1000 cubic feet per minute)[c]	Remarks
Cyclones:					
Single	1-2	15	0.5-3	0.1-0.6	Simple, inexpensive, most widely used
Multiple	3-6	5	2-10	0.5-2	Abrasion and plugging problems
Electrostatic precipitators:					
One-stage	6-30	<0.1	0.1-0.5	0.2-0.6	High efficiency, heavy duty, expensive
Two-stage	2-6	<0.1	0.1-0.3	0.2-0.4	Compact, air conditioning service
Filters:					
Tubular	3-20	<0.1	2-6	0.5-1.5	High efficiency, temperature and humidity limit
Reverse jet	7-12	<0.1	2-6	0.7-1.5	More compact, constant flow
Envelope	3-20	<0.1	2-6	0.5-1.5	Limited capacity, constant flow possible
Scrubbers:					
Spray tower	1-2	10	0.1-0.5	0.1-0.2	Low water use
Jet	4-10	2	-	2-10	Pressure gain, high-velocity liquid jet
Venturi	4-12	1	10-15	2-10	High-velocity gas stream, higher pressure drop (40 to 70 inches) will remove submicron-sized particles
Cyclonic	3-10	5	2-8	0.6-2	Modified dry collector
Inertial	4-10	2	2-15	0.8-8	Abrasion problems
Packed	3-6	5	0.5-10	0.6-2	Channeling problem
Rotating impeller	4-12	2	-	2-10	Abrasion problem

[a]Includes auxiliaries.

[b]With 90-95 percent efficiency (weight).

[c]Includes pressure loss, water pumping, and electrical energy.

Source: American Petroleum Institute, 1978.

TABLE 4-4

PARTICLE COLLECTION EFFICIENCY

Collection Method	Overall Efficiency (percent)	Efficiency at 5μ (percent)	Efficiency at 2μ (percent)	Efficiency at 1μ (percent)
Cyclone, medium-efficiency	65.3	27	14	8
Cyclone; high-efficiency	84.2	73	46	27
Cyclone, irrigated	91.0	87	60	42
Electrostatic precipitator	94.1	92	85	70
Fabric filter	99.9	>99.9	99.9	99
Spray tower	96.3	94	87	55
Scrubber; wet impingement	97.9	97	92	80
Scrubber; self-induced spray	93.5	93	75	40
Scrubber; venturi	99.7	99.6	99	97
Disintegrator	98.5	98	95	91

Source: American Petroleum Institute, 1978.

summarized in Table 4-5. Many of these variables are limiting factors due to equipment or regulatory requirements.

4.2.1.2 Carbon Monoxide Control. The NSPS for FCC unit regenerators require that carbon monoxide emissions not exceed 0.05 percent (volume) of the flue gases. The flue gas from an uncontrolled regenerator typically contains 10 percent carbon monoxide (Murphy and Soudek, 1977). The emission of carbon monoxide is reduced by oxidation to carbon dioxide either in a CO boiler or in the regenerator itself (in situ combustion). The oxidation reaction is exothermic and the heat generated is removed as steam.

Carbon monoxide boilers are generally water wall boilers using carbon monoxide and an auxiliary fuel to maintain firing temperatures of 700°C to 760°C. The oxidation of CO to CO_2 is essentially complete, and FCC regenerators using CO boilers do not have difficulty meeting the NSPS.

Increased particulate matter emissions are permitted from CO boilers using solid or liquid fossil fuels as auxiliary fuel. The increase is calculated from the heat value of the auxiliary fuel as 0.18 gram of particulate matter per million calories of heat input attributable to the auxiliary fuel. An exemption from the particulate matter standard for a six-minute period permits soot blowing from the boiler tubes.

Regenerator in situ combustion of carbon monoxide is achieved by either raising the temperature in the regenerator or by using a CO

TABLE 4-5

EFFECTS OF VARIABLES ON DUST COLLECTION EQUIPMENT

Variable	Cyclones	High-Efficiency Cyclones	Electrostatic Precipitators	Fabric Collectors	Wet Collectors
Effect of Dust Variations:					
Efficiency, particles:					
<1 micron	Poor	Poor	Good	Good	Poor to fair[a]
1-10 micron	Poor	Poor to Fair	Good	Good	Fair to good[a]
10-20 micron	Poor	Good	Good	Good	Good
>20 micron	Fair to Good	Good	Good	Good	Good
Abrasion resistance	Fair	Fair	Good	Good	Good
Ability to handle sticky, adhesive materials	Fair	Poor	Poor	Poor	Poor to good
Bridging materials give trouble	Slight	Yes	Yes	Yes	No
Fire or explosion hazard minimized	Fair	Fair	Poor	Poor	Good
Can handle hygroscopic materials	Yes	Fair	With Care	With Care	Yes
Large foreign materials cause plugging	Seldom	Yes	Yes	Seldom	Seldom to yes
Effect of Gas Stream Variations:					
Maximum temperature (C), standard construction	400	400	400	82-135[b]	No limit
Troubles from condensed or entrained mists or vapors	Slight	Considerable	Some	Considerable	Slight
Corrosive gases attack standard construction	Slight	Slight	Slight	Slight	Severe
Collector:					
Space	Large	Modest	Large	Modest to large	Modest
Pressure drop (inches of water)	1-2 inches	3-5 inches	1-2 inches	2-6 inches	3-6 inches[c]
Reduced volume adversely affects collection efficiency	Yes	Yes with most designs	No	No	Depends on design

[a] Venturi scrubbers are considered good.

[b] Filters for higher temperatures are available.

[c] Pressure drop for venturi scrubbers is in the range of 10 to 70 inches of water.

Source: American Petroleum Institute, 1978.

combustion promoter catalyst. Very often, in situ combustion, which generally requires that the FCC regenerator unit be capable of withstanding continuous operation at 760°C, is not feasible in an older FCC unit regenerator because of metallurgical constraints.

Increasing the temperature in the regenerator has a number of beneficial effects in addition to combustion of coke to carbon dioxide, such as, increased gasoline yields due to greater carbon removal from catalyst, and decreased coke formation on catalyst. The decreased coke formation reduces the overall carbon monoxide and particulate matter emissions from the FCC regenerator unit. It does not affect the ability to meet the particulate matter standard, as the allowable emission is based on coke burn-off. Carbon monoxide emissions have been reported as negligible when using high temperature regeneration (Rheaume et al., 1976a).

Carbon monoxide oxidation catalysts are capable of promoting the oxidation of CO to CO_2 in the regenerator dense bed. In addition, these catalysts increase the yields of gasoline by improving regeneration i.e., reducing the carbon on regenerated catalyst. If these catalysts are added to a regenerator already using high temperature regeneration, the regenerator temperature is reduced. Because the oxidation of CO is exothermic, adding oxidation catalyst to a conventional regenerator will raise the operating temperature. Table 4-6 shows data from three FCC regenerators used to test a CO oxidation

TABLE 4-6

USE OF CARBON MONOXIDE OXIDATION CATALYST

Operating Parameter	Unit A		Unit B		Unit C	
	1	2[a]	3	4[a]	5	6[a]
Regenerator:						
Dense, °C	1325	1303	1336	1326	1156	1296
Dilute, °C	1333	1304	1362	1324	1154	-
Cyclones, °C	1450	1405	1370 1375	1321 1325	1312 1193	1342 1427
Flue gas, °C	1422	1370	-	-	-	-
Flue gas CO, vol %	0	0	3.6	0.3	9.3	0.4
NSPS Standard, vol %	0.05	0.05	0.05	0.05	0.05	0.05

1 - conventional catalyst
2 - CCA-22 with conventional catalyst mixture
3 - CBZ-1 catalyst
4 - CCZ-22 catalyst
5 - DHZ-15 catalyst
6 - CCZ-22 catalyst

[a] CCZ-22 carbon monoxide oxidation catalyst

Source: Rheaume et al., 1976.

catalyst. Carbon monoxide levels were reduced to 0.4 percent or less depending on the operating temperature.

4.2.2 Fuel Gas Combustion Device

The NSPS standard for sulfur dioxide limits the concentration of hydrogen sulfide in fuel gas burned at a refinery. Hydrogen sulfide in fuel gas is controlled by amine stripping and hydrodesulfurization. The standard also permits, as an alternative, the direct removal of sulfur dioxide emissions from the fuel gas burner stack gases. This can be accomplished, for example, by use of wet scrubbers.

Amine gas treating processes include chemical and physical solvent processes and dry absorbent processes. The most common process in petroleum refineries is the diethanolamine (DEA) process (Gary and Handwerk, 1975). In this process, sour refinery gas containing hydrogen sulfide and carbon dioxide contacts DEA in an absorber unit. The hydrogen sulfide and carbon dioxide are removed from the refinery gas and the treated, H_2S-free gas is then used as fuel elsewhere in the refinery. The treated gas will usually contain less than 0.57 gram of sulfur/100 scm of gas (Gary and Handwerk, 1975). The acid-rich DEA solution is regenerated by steam stripping in a regenerator or still. The steam is condensed and the separated H_2S is piped to a sulfur recovery unit. The regenerated DEA is recycled to the absorber unit.

Hydrotreating can be applied at any point in the refinery process stream. It is applied to a wide variety of feedstocks ranging from reduced crude to napthas and is used to stabilize products and/or remove undesirable elements in feedstocks by reaction with hydrogen. Hydrodesulfurization is the removal of sulfur from feedstocks by catalytic reaction with hydrogen. The feedstock is mixed with hydrogen, heated, and passed over a catalyst where the hydrogen reacts with sulfur in the feedstock to form hydrogen sulfide. Excess hydrogen is recovered and recycled and a hydrogen sulfide fuel gas stream is steam distilled from the feedstock. The fuel gas stream is sent to an H_2S removal unit and the desulfurized product is ready for further processing. Any fuel gas generated from further processing will be very low in hydrogen sulfide. Since all products of this feedstock are also low in sulfur, the use of hydrodesulfurization has significant effects outside the refinery.

Wet scrubber technology was discussed previously with regard to the control of particulate matter emissions. The removal of sulfur dioxide from flue gases is the subject of a significant amount of current research. Processes now in commercial use are: ammonia scrubbing, lime-limestone slurry processes, dry limestone processes, and the Wellman-Lord process (sodium sulfite scrubber). At least one proprietary process using an aqueous caustic solution is being used on an FCC unit regenerator (American Petroleum Institute, 1978). There are no known examples of SO_2 scrubbers on process heater exhaust streams.

4.3 Achievable Emission Levels

The emission levels of particulate matter, carbon monoxide, and sulfur dioxide from regenerators and fuel gas combustion devices are discussed in the following section.

4.3.1 Fluid Catalytic Cracker

The emission levels achievable from FCC unit regenerators will be discussed for each of the standards. There is little data within the EPA Regional offices on operational units which have been tested for new source compliance. This is a shortcoming of the present reporting system being used by EPA Regional offices.

4.3.1.1 Particulate Matter. The emission of particulate matter can be controlled to less than the present standard of 1 kg/1,000 kg coke burn-off. However, there is insufficient data to determine the actual effect of cyclone deterioration with time. Table 4-7 shows the currently available compliance test data on particulate matter emissions from FCC regenerators. These data indicate that regenerators equipped with electrostatic precipitators can reduce the emission of particulate matter to 1.0 kg/1,000 kg of coke burn-off. Since electrostatic precipitators are significantly more attractive economically than filter systems or venturi scrubbers, they are considered as the best demonstrated control technology considering cost for the control of particulate matter emissions from FCC regenerators.

The additional particulate matter emission permitted from carbon monoxide boilers is based on data from typical oil or coal-

TABLE 4-7

COMPLIANCE TEST DATA FOR PARTICULATE MATTER

Refinery	Particulate Matter (kg/1000 kg coke burn-off)
Champlin Petroleum Co., Tx. (1977)	
Run #1	1.35
Run #2	0.91
Run #3	0.76
Average	1.01
NSPS Standard	1.0

Source: EPA, 1978.

fired boilers. There is no data to substantiate that emissions can be reduced below this level.

4.3.1.2 Carbon Monoxide. The compliance test data for carbon monoxide emissions from FCC regenerators is shown in Table 4-8. It is apparent from these data that the carbon monoxide boiler is capable of reducing CO emissions to less than 0.004 percent by volume. The use of regenerator in situ combustion of carbon monoxide with or without promoter catalysts can reduce emissions to nearly zero percent if operated at a high enough temperature (Rheaume et al; 1976).

4.3.2 Fuel Gas Combustion Device

The reduction of sulfur dioxide emissions from the combustion of fuel gas is done primarily by removing sulfur from the fuel gas by amine stripping. The available data on achievable concentrations of H_2S in fuel gas are shown in Table 4-9. It is apparent from these data that it is feasible to reduce the H_2S concentration of fuel gas to less than 230 mg/dscm.

4.4 Special Problems Using Control Technologies

4.4.1 Wet Scrubbers

It has been reported that it is not possible to use wet scrubbers in the State of Alaska (EPA, 1978a). Although this could affect compliance with National Ambient Air Standards or possibly state standards for the reduction of sulfur dioxide emissions, this problem should not affect compliance with the current NSPS for petroleum refineries. The best available control technologies considering cost

TABLE 4-8

COMPLIANCE TEST DATA FOR CARBON MONOXIDE

Refinery	Carbon Monoxide (Vol %)
Champlin Petroleum Co., Tx. (1977)	
Run #1	-
Run #2	0.00306
Run #3	0.00353
Average	0.00330
NSPS Standard	0.05

Source: EPA, 1978.

TABLE 4-9

COMPLIANCE TEST DATA FOR SULFUR DIOXIDE

Refinery	H_2S (mg/dscm)
Mobil Oil Co., N.J. (1977)	137
Delta Refining, TN. (1976)	7
Hill Petroleum Co., LA. (1977)	81
Marathon Oil, LA. (1977)	121
Getty Refining, KA. (1976)	65
Standard Oil, CA. (1976)	229*
NSPS Standard	230

*reported as "typical analysis = 0.1 gr H_2S/dscf"

Source: EPA, 1978.

are electrostatic precipitators, either CO boilers or regenerator in situ combustion, and amine strippers. It should, therefore, be possible for petroleum refineries in Alaska to comply with the current NSPS as it is unlikely that climatic conditions will affect these controls.

4.4.2 Condensable Particulates

It has been reported that a significant portion of the particulate matter measured by EPA Reference Method 5 from FCC regenerators using in situ combustion is condensable matter (Huddle, 1978; and EPA, 1978). Since the definition of particulate matter is "...any finely divided solid or liquid material, other than uncombined water, as measured by Method 5 of Appendix A to this part or an equivalent or alternative method" (40 CFR 60.2(V)), the difficulty is not what is collected, but the measurement of the particulate matter catch. The problem appears to be caused by the condensation of sulfuric acid mist in the Reference Method 5 probe and filter. Sulfuric acid mist is very hygroscopic and water of hydration remains with the particulate matter catch after drying. The Champlin Petroleum Company compliance test report (EPA, 1978) states the results of various analytical tests performed on a particulate catch. The results, summarized in Table 4-10, showed that over 50 percent of the measured Reference Method 5 particulate matter catch is other than catalyst fines.

TABLE 4-10

CONDENSABLE PARTICULATES FROM FCC UNIT REGENERATORS

TEST	RESULT
ASME instack filter	89% less particulate matter than Method 5
NaOH titration of Method 5 catch for H_2SO_4	50% H_2SO_4
Thermal analysis of Method 5 catch	60% weight loss
Sulfate analysis of Method 5 catch	64% sulfate
X-ray spectrograph of Method 5 catch	27% H_2SO_4 in probe wash

Source: EPA, 1978.

4.5 Energy Needs and Environmental Effects

Energy consumption has always been a factor in the economics of industrial operations. Today it has become a topic of national concern. Because petroleum refineries use approximately 10 percent of the crude feedstock for energy requirements within the refinery itself, reductions in this energy use are of interest from both an economic and supply viewpoint. Energy consumption in FCC units can be reduced through the use of carbon monoxide oxidation promoter catalysts and energy recovery expansion turbines.

New technologies that will reduce the emission of pollutants to the atmosphere are of national interest. These technologies are of interest to industry as well because of government regulations, environmental concern, and very often, excessive emissions are an indication of inefficient process operations.

4.5.1 Expander Technology

Expander turbines are used to recover some of the energy usually lost in the FCC regenerator flue gas. The amount of energy that is actually recovered is dependent on the inlet gas temperature, gas flow rate, and the pressure drop. Barbier (1977) has estimated that the maximum recovery is approximately 45 kcal/kg of flue gas. In 1973, the largest installation was recovering 15,500 horsepower from a FCC unit installed at a Martinez, California, refinery in 1966 (Braun, 1973). Since that time, expanders as large as 22,000 hp have been installed (C.F. Braun & Co., 1976). Today, an estimated 20,000

hp can be recovered from the average catalytic cracking unit (Oil and Gas Journal, 1977).

Two limiting factors have influenced installation of the energy recovery units. First, erosion of the turbine blades by catalyst fines destroyed early test units. Experiments and commercial experience show that virtually all particulate matter greater than 10 microns must be removed to keep this erosion within acceptable limits (Murphy and Soudek, 1977). The development of third-stage catalyst separators has solved this problem. There is a slight reduction in the efficiency of the turbine due to erosion of the turbine blades with time, but after five years, refineries can expect to recover 95 percent of the energy recovered under the startup conditions (Barbier, 1977).

The other limiting factor is temperature. Present state-of-the-art turbines cannot use gases over 680°C (Barbier, 1977). Since flue gas temperatures from regenerators operating with total in situ combustion can reach 760°C a separator and expander capable of continuous operation at 760°C are required. Without this capability, gases must be cooled before passing through the expander.

The power recovered by the expander is generally used for the FCC unit air blower. Any excess power is used to generate electricity for use at the refinery. Yearly savings of $685,000 were obtained at the Shell Oil Company refinery at Martinez, California. This level of savings yields a 1.8 year payout on a $1.25 million investment (Braun, 1973).

4.5.2 Carbon Monoxide Oxidation Catalysts

Carbon monoxide oxidation catalysts were introduced in the early 1970's as an alternative to the zeolite catalysts being used in fluid catalytic crackers. Typical of these catalysts are the partial combustion zeolite (PCZ) and complete combustion zeolite (CCZ) series catalysts offered by W.R. Grace and Company, Davison Chemical Division. During their first commercial trial in April 1975, CCA-44 was charged to a FCC unit operating with high-temperature regeneration. It is estimated that there are now (1978) 12 FCC units using CO oxidation catalysts and 12 more using CO oxidation additives (Wallendorf, 1978).

The PCZ catalysts promote partial combustion of carbon monoxide with an increase of 17°C to 28°C in the regenerator and are particularly useful where the metallurgy of the regenerator limits the allowable operating temperature. Where the temperature increase is not a limiting factor, CCZ catalysts can be used to promote complete combustion of carbon monoxide in the dense bed with a regenerator temperature increase of approximately 56°C. This increase in regenerator operating temperature is generally accompanied by a reduced cyclone temperature since CO oxidation no longer occurs in the cyclones. Only in the case of replacing catalysts under conventional regeneration conditions with CCZ catalysts is the temperature increased in both the regenerator bed and cyclones.

The advantages of using CO oxidation catalysts are:

- Reduced cyclone temperatures when operating with regenerator in situ combustion since the oxidation reaction is held in the regenerator dense bed.

- Reduced excess air requirements because burning is promoted in the dense bed and increased catalyst activity promotes more efficient use of air. The reduced air requirements should decrease the gas volume through the cyclones, and the increased catalyst activity permits the reduction of catalyst circulation rates. The combination of these effects should reduce the erosion of the cyclone because of decreased gas volume and particle loading.

- Decreased coke on the regenerated catalyst due to burning off more of the coke formed in the reactor and reducing the amount of coke formed in the first place. The less coke on the catalyst, the higher the catalytic activity and the greater the yield of useful products. PCZ and CCZ catalysts are approximately 40 and 150 times more active, respectively, than conventional catalysts (Rheaume et al., 1976).

- The use of torch oil may be discontinued. Torch oil is often used in the regenerator to maintain the high temperature required for in situ carbon monoxide combustion.

- The emission of carbon monoxide is reduced although the actual emissions are dependent on the temperature maintained in the regenerator.

The only disadvantage to the use of carbon monoxide oxidation catalysts is on those FCC units presently using a CO boiler. The heat value of the carbon monoxide must be made up using an alternate fuel.

4.5.3 Sulfur Dioxide Catalysts

Some of the sulfur in the FCC feedstock is retained in the coke on the surface of the catalyst during the cracking process. Steam stripping is used to remove entrained hydrocarbons from this

deactivated catalyst prior to regeneration. This leaves a sulfur/coke covered catalyst for regeneration. During the regeneration process, the coke is oxidized to CO and CO_2, and the sulfur to SO_x, primarily SO_2. The sulfur content of the coke is directly related to the sulfur content of the feed. It is estimated that uncontrolled emissions of SO_x from FCC unit regenerators in the U.S. average 805 ppm and may be as much as 2,750 ppm when high-sulfur feed is processed (Vasalos et al., 1977).

Amoco Oil Company has developed a new UltraCat cracking process which reduces sulfur oxide emissions from FCC unit regenerators. The process uses a new catalyst that retains sulfur oxides on the catalyst and returns them to the reactor where they are removed with the product stream. If a low sulfur product is required, the sulfur will be removed by amine stripping or hydrotreating and eventually recovered in a sulfur recovery unit. Pilot tests indicate that the new catalyst is capable of reducing sulfur oxide emissions 80 to 90 percent and commercial tests are planned to confirm this data (Vasalos et al., 1977).

5.0 INDICATIONS FROM TEST RESULTS

5.1 Test Coverage in Regions

In January of 1978, the Metrek Division of MITRE Corporation made a survey of the NSPS compliance test data available at EPA Regional offices (Watson et al., 1978). The Compliance Data System (CDS) indicated a total of thirteen tests; however, data were available for only nine. There were no reported failures of compliance tests. The Champlin Petroleum Refinery, Corpus Christi, particulate matter test is questionable. EPA Region VI has indicated that no retest is scheduled pending review of the actual method used when taking the third particulate sample (lowest measured level of particulate matter) and results of continuous monitoring in the future.

The NSPS compliance test data for petroleum refineries that is available at the EPA Regional offices is presented in Table 5-1. There is one particulate matter test at 1.01 kg/1,000 kg coke burnoff, no opacity data, one carbon monoxide test at 0.0033 percent, and seven hydrogen sulfide tests with averages ranging from a low concentration of 1.4 mg H_2S/dscm fuel gas to a high of 228.8 mg H_2S/dscm fuel gas. There are indications in the CDS system that four additional tests have been performed but the data were not available. This indicates that a total of 13 tests have been performed (Watson et al., 1978).

The data presented in Table 5-2 is presented in contrast to this figure of thirteen NSPS compliance tests. This table shows the

TABLE 5-1

NSPS COMPLIANCE TEST DATA - PETROLEUM REFINERIES

EPA Region	Indicated Total Number of Tests Performed	NSPS Data							
		Particulate Matter ($kg/10^3$ kg coke burnoff)		Opacity (%)		Carbon Monoxide (ppm)		Sulfur Dioxide (mg H_2S/dscm)	
		Range	Average	Range	Average	Range	Average	Range	Average
Region II	3								
Mobil Oil, Paulsboro, N.J.								<2.3-3.9	1.4
Region IV	1								
Delta Refining, Memphis, TN								3.7-14.0	7.3
Region V	1								
Region VI	3								
Champlin Petroleum, Corpus Christi, TX		0.76-1.35	1.01			30.6-35.3	33	58.3-110.5	80.8
Hill Petroleum, Krotz Springs, LA								99.4-157.1	120.6
Marathon Oil, Garyville, LA									
Region VII	2								
Getty Refining, El Dorado, KA								42.3-73.5	64.5
Region IX	1								
Chevron U.S.A., El Segundo, CA								50.8-117.4	80.0
Scandard Oil, Richmond, CA									228.8
Current NSPS			1.0		30		500		230

Source: Watson et al., 1978.

TABLE 5-2

GEOGRAPHIC DISTRIBUTION OF POSSIBLE NSPS AFFECTED FACILITIES

EPA Region	Number of New or Increased Capacity Fluid Catalytic Cracker Units			Number of Facilities Reported by Regional Offices[c]		
	Completed[a] ('975-78/cap.[d])	Under Construction[b] (comp. date)	Engineering[b] (comp. date)	Fluid Cat Cracker (FCC)	Fuel Gas Combustor (FGC)	Future Sources (FCC/FGC)
I	-	-	-	-	-	-/1P
II	1/10	1(80)		-	3	-/-
III	4/15	-	1(NA)	-	-	-/-
IV	-	-	1(79)	-	2	-/-
V	11/86	-	1(NA)	-	1	-/-
VI	16/149	1(NA) 1(77) 1(79)	1(78) 6(79)	1	38	1U, 1P/38U, 37P
VII	4/4	1(79)	-	-	6	-/-
VIII	7/6	1(78)	1(78)	-	6	e
IX	6/112	-	-	f	f	f
X	1/3	-	-	-	6	-/1P
Total	50/385	1(77) 1(78) 2(79) 1(80) 1(NA)	2(78) 7(79) 2(NA)	1	62	1U, 1P/38U, 39P

[a]Cantrell, 1975.

[b]Hydrocarbon Processing, 1978; data as of 1 January 1978.

[c]Watson et al., 1978. (U - under construction; P - planned)

[d]Capacity in 10^3 barrels per stream day.

[e]CDS file does not show any sources planned or under construction. Use of these entries varies among the Regions. It should not be assumed that no new sources are planned or are under construction in this Region.

[f]Not available.

distribution of possible NSPS affected facilities. The EPA Regional offices have reported that there are two NSPS affected FCC units and 62 fuel gas combustion devices (Watson et al., 1978). A literature search shows that fifty refineries have built new FCC units or increased FCC unit capacity during the period 1975-1978 (Cantrell, 1975; 1978).* Data on fuel gas combustion sources is not available. It is not within the scope of this project to determine which facilities are, in fact, subject to the NSPS.

In addition to the data on present NSPS affected facilities, Table 5-2 presents information on the geographic distribution of the growth of these sources. The EPA Regional offices reported one FCC unit under construction and one being planned (Watson et al., 1978). Hydrocarbon Processing (1978) on the other hand reports six FCC units under construction (new or being modified/revamped to increase capacity) and eleven more in the engineering phase.** Again this data is presented for further consideration for a determination of which, if any, of these FCC units might be considered affected facilities and hence subject to the NSPS.

*See Appendix A for details on which refineries have reported growth during this period.

**See Table 4-2 for details on refineries reporting future growth plans.

5.2 Analysis of Test Results

There is insufficient compliance test data in CDS to make a judgement on the adequacy of the present NSPS for petroleum refineries. The available compliance test data presented indicates that:

- The particulate matter standard is compatible with the present state of control technology.
- The opacity standard, which was set to match the mass standard, is compatible with the present state of control technology.
- The carbon monoxide standard could be changed to reduce the allowable emission of carbon monoxide although the present data are insufficient to establish an appropriate standard.
- The sulfur dioxide standard could also be changed to reduce the allowable concentration of hydrogen sulfide in fuel gas although more data should be collected which will relate the H_2S reduction achievable to the sulfur content of feedstocks.

6.0 ANALYSIS OF POSSIBLE REVISIONS TO THE STANDARD

This section will approach the analysis of possible revisions to the NSPS by examining the emission of particulate matter, carbon monoxide, suliur dioxide, and hydrocarbons. The analysis consists of an examination of the available data in light of environmental, economic, control technology, and process effects.

6.1 Particulate Matter

There is insufficient data to support a change to the present particulate matter standard. New control technologies have been developed that can reduce the emission of particulate matter effectively, but not to a sufficient degree to justify a change in the NSPS of 1 kg particulate matter per 1,000 kg of coke burn-off.

Technological trends in the industry do not appear to significantly affect the particulate matter standard. These trends include the use of higher temperature reactors and regenerators, and new catalysts and/or additives. The actual quantity of particulate matter emitted will be affected by a reduction in the quantity of coke formed on the catalyst and a reduction in catalyst flow rates, thereby reducing catalyst and carbon emissions. This reduction does not affect the present standard because allowable emissions are based on the quantity of coke burned off the catalyst.

The particulate matter emitted from a FCC unit regenerator consists primarily of catalyst fines produced in the first stage cyclone. Additional particulate matter is the result of chemical reactions in

the flue gas which result in the formation of condensable sulfates. The particles range in size from 0.5 micron to 60 microns in diameter with as much as 86 percent of these particles greater than 10 microns in diameter (Balfoort, 1976). As a result, a number of control technologies are suitable for reducing the emission level, but present data show that electrostatic precipitators are the best demonstrated control technology considering cost for minimizing the final emission level. Only filters are as efficient at removing small particles as electrostatic precipitators. Wet scrubbers, which have the potential for efficient small particle removal, also have the added advantage (from an environmental viewpoint) of removing sulfur compounds.

The measurement of particulate matter requires the use of Reference Method 5 or its equivalent. It has been recognized in the past that condensable particulate matter will collect in the impingers of the Method 5 sampling train. This material is not included in the reportable particulate matter catch. It was also recognized that condensable particles were being collected in the sampling probe and on the filter (EPA, 1975). These particles are reportable as particulate matter. Most of these condensable particles are believed to be sulfuric acid mist, a highly hygroscopic material, and other sulfates. Because of this, it is difficult to actually be assured of the quantity of catalyst fines, condensable particles, and moisture being measured. At present, all this material is, by definition, particulate matter.

There are no CDS opacity data to comment on. The fact that there is no requirement to record mass emissions and opacity at the same time is a shortcoming. There is no reason to require mass emission testing whenever opacity is measured, but the reverse would result in the availability of significant data on the relationship of opacity and mass emissions from FCC regenerators.

The particulate matter standard was set at a higher level than can be attained in newly installed FCC unit regenerator systems. This was done in recognition of the fact that the systems are normally operated continuously for up to two years or longer without a major shutdown. The internal cyclones are inaccessable for maintenance during the period and because of erosion, emissions tend to increase (EPA, 1973b). It is possible that particulate emissions could be maintained at a lower level through the use of an additional high efficiency separator external to the regenerator but upstream of the precipitator. This separator is reported to be less prone to erosion, and, because it is external to the regenerator, is more accessable for maintenance. The efficiency of the separator is dependent on the efficiency of the cyclones preceding it. This efficiency change is due primarily to the size distribution of the particles in the inlet stream. Efficient cyclones change the size distribution of the particles in the separator inlet stream and therefore reduce the separator efficiency. Separator efficiencies range

from approximately 70 percent to over 90 percent in units with highly efficient internal cyclones to poor cyclones, respectively (Krueding, 1975).

6.2 Carbon Monoxide

The NSPS for carbon monoxide can be met by the use of a waste heat boiler which not only controls emissions but recovers the heat value of the oxidation reaction of carbon monoxide to carbon dioxide. The other commonly used control technology is combustion of the carbon monoxide in the regenerator itself. The advantages of in situ regeneration are: increased yields of useful products, decreased emissions of particulate matter, and recovery of waste heat in an energy expander. There is no CDS data on the carbon monoxide emissions from a regenerator using regenerator in situ combustion of carbon monoxide.

In the past, the metallurgy of the regenerator and cylones was a limiting factor which determined those FCC units capable of operating with high temperature in situ combustion. The recent development of carbon monoxide oxidation catalysts and additives has permitted many units to at least partially, and often completely, oxidize carbon monoxide in the regenerator without resorting to high temperatures. Little data are available on the emission level of carbon monoxide from FCC unit regenerators using CO oxidation promotors. An additional advantage of using the oxidation promoter over conventional high temperature regeneration is that the

oxidation reaction remains in the dense bed, the cyclone temperature is reduced, and presumably erosion and particulate matter emissions will be reduced. There is no data as yet to substantiate the last conclusion, although it is reasonable.

6.3 Sulfur Dioxide

The present NSPS for sulfur dioxide limits the concentration of hydrogen sulfide in fuel gas burned in a petroleum refinery to 230 mg H_2S/dscm of fuel gas. There is provision for the refinery owner/operator to reduce sulfur dioxide emissions in flue gas instead of hydrogen sulfide in fuel gas. The CDS data that were available at the EPA Regional offices indicate that refineries are presently reducing the concentration of H_2S in fuel gas to levels substantially below the present NSPS. There were no data to indicate by what amount the H_2S concentration was being reduced (efficiency of the controls) nor how the H_2S concentration related to the sulfur content of the feedstock.

According to Gary and Handwerk (1975), amine gas treating units usually reduce sulfur concentrations to less than 5.72 mg/dscm. The concentration of H_2S in treated fuel gas reported in the CDS files ranges from less than 7 mg/dscm to 229 mg/dscm (Watson et al., 1978). Although the compliance test data show concentrations significantly above the concentration reported in Gary and Handwerk, most of these measurements are still substantially below the 230 mg/dscm maximum concentration allowed by the NSPS.

Presently, there is no NSPS for sulfur dioxide emissions from the fluid catalytic cracker regenerator nor from the regenerator incinerator waste-heat boiler. The FCC unit regenerator emissions of sulfur oxides are estimated at 2.3×10^8 to 3.9×10^8 kg/yr based on current FCC capacity and emission factors from the EPA (1973). In addition, there are additional sulfur oxide emissions from the regenerator waste heat boiler due to the use of auxiliary fuel. The actual quantity of emissions depends on the sulfur content of the auxiliary gaseous, liquid, or solid fuel. Even if fuel gas is used as the auxiliary fuel, there are no requirements to control SO_x as the boiler has been exempted from the sulfur dioxide standard for fuel gas combustion devices.

State air pollution standards (1976) for SO_x from new source FCC unit regenerators range from 440 ppm to 2,000 ppm in the flue gas. However, the actual achievable emission rate is dependent on feedstock, feedstock sulfur content, and other process variables. If the feedstock is low in asphaltenes, hydrodesulfurization may have the capability to reduce the sulfur oxide emission rate. Process variables such as high temperature regeneration and the use of SO_x recycle catalysts may also be capable of reducing the level of SO_x emitted from the regenerator. Data are not available to specify the actual levels of these emissions.

6.4 Hydrocarbons

The emission of hydrocarbons from FCC unit regenerators is not addressed in the present NSPS. There is a great interest in hydrocarbons because of the relationship of many of these compounds with health hazards and the formation of smog. A number of potentially hazardous hydrocarbons are known to be present in the flue gas from an uncontrolled FCC unit regenerator. Table 6-1 lists some of the hydrocarbons which are known to be hazardous and are known to be present in the regenerator flue gas stream. Of particular concern are the polynuclear aromatics (PNA's) because of their potential carcinogenic effects. The most abundant PNA in regenerator flue gas is benzo-a-pyrene (BAP) with a concentration of 0.218 kg BAP/1,000 barrels of feed. The concentration of BAP can effectively be reduced in a carbon monoxide boiler to 1.41×10^{-5} kg BAP/1,000 barrels of feed (Arthur D. Little, Inc., 1976). There are no data to determine the concentration of BAP in the flue gas from high temperature (in situ) regeneration nor in the case of regenerators using CO oxidation promoting catalysts.

TABLE 6-1

HAZARDOUS HYDROCARBONS EMITTED FROM FCC UNIT REGENERATORS

Hydrocarbons	Concentration (ppm)
Aldehydes (as H_2CO)	3 - 130
Cyanides (as HCN)	0.19 - 0.94
Anthracene	2,070[a]
Pyrenes	40 - 28,000[a]
Benzo (ghi) perylenes	15 - 424[a]
Benzo (a) pyrene	4 - 460[a]
Benzo (e) pyrene	11 - 3,600[a]
Phenanthrenes	400,000

[a] Micrograms per barrel of oil charged

Source: Bombaugh et al., 1976.

7.0 CONCLUSIONS

7.1 Particulate Matter

The available data do not support any changes to the present NSPS. New technologies such as high efficiency separators, high temperature regeneration, and new catalysts have reduced the total quantity of particulate matter emitted. The method of calculating the allowable emissions has already corrected for the reduction due to changes in catalysts and operating procedures. The current standard remains valid.

The Reference Method 5 for measuring particulate matter emissions continues to be controversial because the temperature of the sampling train affects the amount of condensable particles present in the measured particulate matter.

7.2 Carbon Monoxide

The NSPS for carbon monoxide emissions was based on the use of regenerator in situ combustion. This method of controlling carbon monoxide emissions is less effective than a carbon monoxide boiler. There are insufficient data to substantiate any change in the original finding that it is not practical to control CO emissions to less than 500 ppm by in situ regeneration. The recent advent and increased use of CO oxidation catalysts and additives may have altered that original finding although no compliance test data were found to substantiate this.

7.3 Sulfur Dioxide

A number of conclusions regarding the present NSPS for sulfur

dioxide have been discussed previously, namely:

- Compliance with the present standard is difficult to ensure without a continuous monitoring method.
- Compliance test data indicates that a reduction in the allowable concentration of hydrogen sulfide in fuel gas is possible.
- The present standard for fuel gas combustion devices has excluded regenerator waste-heat boilers even though they may, in fact, generate and emit SO_x when using fuel gas as an auxiliary fuel.
- Although a separate standard for particulate matter was promulgated for regenerator waste heat boilers using liquid or solid fossil fuel, no standard applies to the SO_x generated when these fuels are used. This should be examined if the SO_x standard is revised for fuel gas combustion devices or a standard is developed for FCC unit regenerators.
- The FCC unit regenerator emits significant quantities of sulfur oxides which are presently uncontrolled. Control technologies for the reduction of sulfur dioxide emissions from other industries exist and may be applicable to FCC regenerators, and, in fact, there are FCC regenerators with SO_x emission controls. At least ten states have a sulfur oxide emission limit for FCC regenerators which apply to existing and new sources and may be a source of data on the applicability of SO_x control devices.
- Little is known of the actual effect of an increased sulfur content of feedstocks on the emission of sulfur oxides from the regenerator. Refineries are being forced to process a higher sulfur content feed due to shortages of domestic crude and this will have an effect on the final emission level as well as on the ability to control the emissions.

7.4 Hydrocarbons

There is not enough known about the emission of hydrocarbons from FCC units to justify setting a standard. The present data however indicate that: the uncontrolled emissions are significant, they depend on the process, and because of potential adverse health effects, they may require control.

8.0 RECOMMENDATIONS

The following recommendations are made regarding the NSPS for particulate matter, carbon monoxide, sulfur dioxide, and hydrocarbons.

8.1 Particulate Matter

- Do not change the present standard of 1.0 kg/1,000 kg coke burn-off and 30 percent opacity.
- Reevaluate the Reference Method 5 for particulate matter.
- Require that opacity be measured when mass loading tests are made.

8.2 Carbon Monoxide

- Collect data to ascertain the level of carbon monoxide emissions from high temperature (in situ) regenerators with and without the use of CO oxidation catalysts and additives.
- Reevaluate the carbon monoxide standard in light of the findings from the above research.

8.3 Sulfur Dioxide

- Change the definition of a fuel gas combustion device to include the regenerator incinerator-waste heat boiler by deleting the exemption.
- Develop a continuous monitoring method for hydrogen sulfide.
- Reevaluate the present standard in light of the effect of an increased sulfur content of feedstock on the concentration of hydrogen sulfide in fuel gas and of current compliance test data on achievable levels of hydrogen sulfide in fuel gas.
- Investigate FCC unit regenerator sulfur oxide control technology, including cost, performance, applicability, effect of feed stocks, etc. Subject to the findings of such an investigation, develop a standard for sulfur dioxide emissions from FCC unit regenerators.

8.4 Hydrocarbons

- Evaluate the effect of: conventional regeneration, CO boilers, high temperature regeneration, and regeneration with CO combustion catalysts and additives on the emission of hydrocarbons from FCC unit regenerators.

- Assess the need for the regulation of hydrocarbon emissions from FCC unit regenerators based on results from the above research.

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APPENDIX A

REPORTED FLUID CATALYTIC CRACKING UNITS AT PETROLEUM REFINERIES

APPENDIX A
REPORTED FCC UNITS AT PETROLEUM REFINERIES

EPA Region	Company/City	FCC Capacity (Mb/sd) 1975[a]	1978[b]	Change*
Region I:				
Connecticut	None reported			
Maine	"			
Massachusetts	"			
New Hampshire	"			
Rhode Island	"			
Vermont	"			
	Subtotal:	-	-	-
Region II:				
New Jersey	Exxon, Linden	125	135	10
	Texaco, Westville	40	40	0
New York	Ashland, North Tonawanda	22	22	0
	Subtotal:	187	197	10
Region III:				
Delaware	Getty, Delaware City	62	62	0
Maryland	None reported	-	-	-
Pennsylvania	BP, Marcus Hook	40	48	8
	Gulf, Philadelphia	80	84.6	4.6
	Sun, Marcus Hook	75	75	0
	United, Warren	10	11.5	1.5
Virginia	Amoco, Yorktown	27	28	1
West Virginia	None reported	-	-	-
	Subtotal:	294	309.1	15.1

*Increase/(decrease) in FCC capacity

†Change in ownership

§Reported in Mb/cd, Mb/sd calculated
(Mb/cd - thousand barrels per calendar day, Mb/sd - thousand barrels per stream day)

Sources:

[a]Cantrell, 1975.

[b]Cantrell, 1978.

REPORTED FCC UNITS AT PETROLEUM REFINERIES

EPA Region	Company/City	FCC Capacity (Mb/sd) 1975[a]	1978[b]	Change*
Region IV:				
Alabama	None reported	-	-	-
Florida	"	-	-	-
Georgia	"	-	-	-
Kentucky	Ashland, Catlettsburg	54	54	0
	Ashland, Louisville	10.5	10	(0.5)
Mississippi	Chevron, Pascagoula	-	56	56†
	Standard of Kentucky, Pascagoula	56	-	(56)†
North Carolina	None reported	-	-	-
South Carolina	"	-	-	-
Tennessee	"	-	-	-
	Subtotal:	120.5	120	(0.5)
Region V:				
Illinois	Amoco, Wood River	38	38	0
	Clark, Blue Island	24	26	2
	Clark, Hartford	26	26	0
	Marathon, Robison	36.5	36.5	0
	Mobil, Joliet	66	92	26
	Shell, Wood River	94	94	0
	Texaco, Lawrenceville	31	34	3
	Texaco, Lockport	30	30	0
	Union of CA, Lemont	54	55	1
Indiana	Amoco, Whiting	118	140	22
	Atlantic Richfield, East Chicago	48	-	(48)†
	Energy Coop, East Chicago	-	48	48†
	Indiana Farm Bureau, Mt. Vernon	6.1	6.3	0.2
	Rock Island, Indianapolis	15	17	2
Iowa	None reported			
Michigan	Marathon, Detroit	21.5	25.5	4
	Total Leonard, Alma	12	-	(12)†
	Total Petroleum, Alma	-	16	16†
Minnesota	Continental, Wrenshall	9.5	9.5	0
	Koch, Pine Bend	24	-	(24)†
	Koch, Rosemont	-	45	45†
	Northwestern, St. Paul Park	21	22	1
Wisconsin	Murphy, Superior	9.7	9.7	0
	Subtotal:	684.3	770.5	86.2

*Increase/(decrease) in FCC capacity

†Change in ownership

§Reported in Mb/cd, Mb/sd calculated
(Mb/cd - thousand barrels per calendar day, Mb/sd - thousand barrels per stream day)

Sources:

[a]Cantrell, 1975.

[b]Cantrell, 1978.

REPORTED FCC UNITS AT PETROLEUM REFINERIES

EPA Region	Company/City	FCC Capacity (Mb/sd) 1975[a]	1978[b]	Change*
Region VI:				
Arkansas	Lion Oil Co., Eldorado	15	15	0
Louisiana	Cities Service, Lake Charles	125	125	0
	Exxon, Baton Rouge	163	169	6
	Good Hope Ref., Good Hope	15	17	2
	Gulf, Belle Chasse	78	78	0
	Murphy, Meraux	10.5	10.5	0
	Shell, Norco	100	100	0
	Tenneco, Chalmette	22	22	0
	Texaco, Convent	70	70	0
New Mexico	Shell Oil, Ciniza	7.2	7.2	0
Oklahoma	Apco, Cyril	6	6.7	0.7
	Champlin, Enid	19.5	19	(0.5)
	Continental, Ponca City	44	44	0
	Hudson, Cushing	-	7	7†
	Kerr-McGee, Wynnewood	11.5	11.5	0
	Midland, Cushing	7	-	(7)†
	Sun, Duncan	25	25	0
	Sun, Tulsa	30	30	0
	Texaco, West Tulsa	18§	18§	0
	Vickers, Ardmore	13	21.5	8.5
Texas	American, Port Arthur	30	32	2
	Amoco, Texas City	135	167	32
	Atlantic Richfield, Houston	69	74	5
	Champlin, Corpus Christi	10	54	44
	Charter, International, Houston	24	37.5	13.5
	Chevron, El Paso	22	22	0
	Coastal States, Corpus Christi	19	19	0
	Cosden, Big Spring	24	24	0
	Crown Central, Houston	43	43	0
	Exxon, Bay town	124	135	11
	Gulf, Port Arthur	120	120	0
	La Gloria, Tyler	10	10	0
	Marathon, Texas City	28.5	30	1.5
	Mobil, Beaumont	80	90	10
	Phillips, Borger	55	56	1
	Phillips, Sweeny	30	34	4
	Shell, Deer Park	70	70	0
	Shell, Odessa	10.5	10.5	0
	Southwestern, Corpus Christi	9.5	12	2.5
	Suntide, Corpus Christi	20	-	(20)†
	Sun, Corpus Christi	-	25	25†
	Texaco, Amarillo	8§	8§	0
	Texaco, El Paso	7§	7§	0
	Texaco, Port Arthur	135§	135§	0
	Texas City, Texas City	27	27	0
	Union of Calif., Nederland	40	-	(40)†
	Union of Calif., Beaumont	-	39	39†
	Winston, Fort Worth	3.4	3.4	0
	Subtotal:	1933.6	2080.8	147.2

*Increase/(decrease) in FCC capacity

†Change in ownership

§Reported in Mb/cd, Mb/sd calculated
(Mb/cd - thousand barrels per calendar day, Mb/sd - thousand barrels per stream day)

Sources:

[a]Cantrell, 1975.

[b]Cantrell, 1978.

REPORTED FCC UNITS AT PETROLEUM REFINERIES

EPA Region	Company/City	FCC Capacity (Mb/sd) 1975[a]	1978[b]	Change*
Region VII:				
Kansas	American Petroleum, El Dorado	11	-	(11)†
	APCO, Arkansas City	9.2	9.6	0.4
	CRA, Coffeyville	14.5	16	1.5
	CRA, Phillip	7	8.5	1.5
	Derby, Wichita	10.8	10.8	0
	Getty, El Dorado	-	17	17†
	National Coop, McPherson	20	20	0
	Pester, El Dorado	-	11	11†
	Phillips, Kansas City	32	32	0
	Skelly, El Dorado	31	-	(31)†
	Amoco, Sugar Creek	41	41	0
Missouri	CRA, Scotts Bluff	2.4	2.4	0
Nebraska	Ashland, Canton	24.5	24.5	0
Ohio	Gulf, Toledo	20	19.8	(0.2)
	Gulf, Cleves	18	18	0
	Standard of Ohio, Lima	37	37.7	0.7
	Standard of Ohio, Toledo	55	55	0
	Sun of Pennsylvania, Toledo	50	50	0
	Subtotal:	383.4	373.3	(10.1)
Region VIII:				
Colorado	Asamera, Commerce City	-	7	7†
	Continental, Commerce City	14	15	1
	The Refinery Corp., Commerce City	7.6	-	(7.6)†
	Cenex, Laurel	10.5	12	1.5
Montana	Continental, Billings	14	15	1
	Exxon, Billings	19	19.2	0.2
	Phillips, Great Falls	1.8	1.8	0
	Amoco, Mandan	23	23	0
North Dakota	None reported	-	-	-
South Dakota	Amoco, Salt Lake City	17	18	1
Utah	Chevron, Salt Lake City	10	11	1
	Major, Roosevelt	5	-	(5)††
	Plateau, Roosevelt	-	5.2	5.2†
	Amoco, Casper	9.5	9.4	(0.1)
Wyoming	Husky, Cheyenne	10	10	0
	Husky, Cody	3.3	3.3	0
	Pasco, Sinclair	17.7	-	(17.7)††
	Sinclair, Sinclair	-	17.7	17.7†
	Texaco, Casper	7	7	0
	Subtotal:	169.4	174.6	5.2

*Increase/(decrease) in FCC capacity

†Change in ownership

§Reported in Mb/cd, Mb/sd calculated
(Mb/cd - thousand barrels per calendar day, Mb/sd - thousand barrels per stream day)

Sources:

[a]Cantrell, 1975.

[b]Cantrell, 1978.

REPORTED FCC UNITS AT PETROLEUM REFINERIES

EPA Region	Company/City	FCC Capacity (Mb/sd) 1975[a]	1978[b]	Change*
Region IX:				
Arizona	None reported	-	-	-
California	Atlantic Richfield, Carson	57	56	(1)
	Chevron, El Segundo	-	47	47
	Chevron, Richmond	-	55	55
	Exxon, Benecia	45	46	1
	Gulf, Santa Fe Springs	13.5	13.5	0
	Mobil, Torrance	56	60	4
	Phillips, Avon	47	-	(47)†
	Powerine Oil, Sante Fe Springs	11	11.5	0.5
	Shell Oil, Martinez	46	46	0
	Shell Oil, Wilmington	35§	35§	0
	Texaco, Wilmington	28§	28§	0
	Tosco Corp., Lion Oil, Avon	-	47	47†
	Union Oil of Calif., Los Angeles	45	45	0
Hawaii	Chevron, Barbers Point	-	19	19†
	Standard of Calif., Barbers Point	14.1	-	(14.1)†
Nevada	None reported	-	-	-
	Subtotal:	397.6	509	111.4
Region X:				
Alaska	None reported	-	-	-
Idaho	"	-	-	-
Oregon	"	-	-	-
Washington	Shell, Anacortes	36§	36§	0
	Texaco, Anacortes	27§	30§	3
	Subtotal:	63	66	3
GRAND TOTAL		4232.8	4600.3	367.5

*Increase/(decrease) in FCC capacity

†Change in ownership

§Reported in Mb/cd, Mb/sd calculated
(Mb/cd - thousand barrels per calendar day, Mb/sd - thousand barrels per stream day)

Sources:

[a]Cantrell, 1975.

[b]Cantrell, 1978.